Chapter 3

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pH Meter

GMDN Code	15164
ECRI Code	15-164
Denomination	pH Meter

The pH meter is used for determining the concentration of hydrogen ions [H^+] in a solution. This equipment, provided it is carefully used and calibrated, measures the acidity of an aqueous solution. pH meters are sometimes called pH analysers, pH monitors or potentiometers.
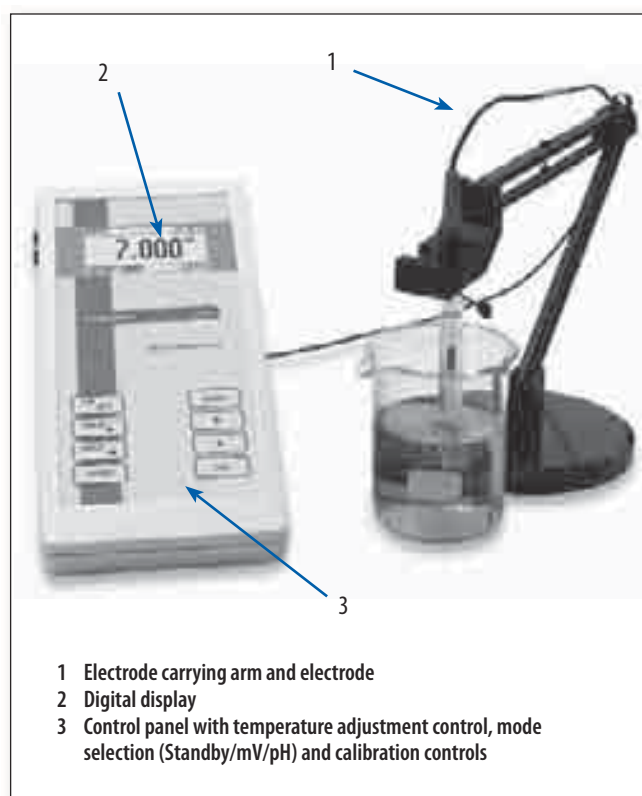
PURPOSE OF THE EQUIPMENT

The pH meter is commonly used in any field of science related to aqueous solutions. It is used in areas such as agriculture, water treatment and purification, in industrial processes such as petrochemicals, paper manufacture, foods, pharmaceuticals, research and development, metal mechanics, etc. In the health laboratory, its applications are related to the control of culture mediums and to the measurement of the alkalinity or acidity of broths and buffers. In specialized laboratories, diagnostic equipment microelectrodes are used to measure the pH of liquid blood components. The plasma pH allows the patient's health to be evaluated. It normally measures between 7.35 and 7.45. This value relates to the patient's metabolism in which a multitude of reactions occurs where acids and bases are normally kept in balance. Acids constantly liberate hydrogen ions [H^+] and the organism neutralizes or balances acidity by liberating bicarbonate ions [HCO_3^-]. The acid-base ratio in the organism is maintained by the kidneys, (organs in which any excesses present are eliminated). The plasma pH is one of the characteristics that vary with factors such as age or state of health of the patient. Table 1 shows typical pH values of some bodily fluids.

pH values of some bodily fluids

Fluid	pH Value
Bile	7.8 – 8.6
Saliva	6.4 – 6.8
Urine	5.5 – 7.0
Gastric Juice	1.5 – 1.8
Blood	7.35 – 7.45

PHOTOGRAPH AND COMPONENTS OF THE pH METER

Photo courtesy of Consort

1 Electrode carrying arm and electrode
2 Digital display
3 Control panel with temperature adjustment control, mode selection (Standby/mV/pH) and calibration controls

OPERATION PRINCIPLES

The pH meter measures the concentration of hydrogen ions [H^+] using an ion-sensitive electrode. Under ideal conditions, this electrode should respond in the presence of only one type of ion. In reality, there are always interactions or interferences with other types of ions present in the solution. A pH electrode is generally a combined electrode, in which a reference electrode and an internal glass electrode are integrated into a combined probe. The lower part of the probe ends in a round bulb of thin glass where the tip of the internal electrode is found. The body of the probe

contains saturated potassium chloride (KCl) and a solution 0.1 M of hydrogen chloride (HCl). The tip of the reference electrode's cathode is inside the body of the probe. On the outside and end of the inner tube is the anodized end. The reference electrode is usually made of the same type of material as the internal electrode. Both tubes, interior and exterior, contain a reference solution. Only the outer tube has contact with the measured solution through a porous cap which acts as a saline bridge.

This device acts like a galvanized cell. The reference electrode is the internal tube of the pH meter probe, which cannot lose ions through interactions with the surrounding environment. Therefore as a reference, it remains static (unchangeable) during the measuring process. The external tube of the probe contains the medium which is allowed to mix with the external environment. As a result, this tube must be filled periodically with a potassium chloride solution (KCl) for restoring the capacity of the electrode which would otherwise be inhibited by a loss of ions and evaporation.

The glass bulb on the lower part of the pH electrode acts as a measuring element and is covered with a layer of hydrated gel on its exterior and interior. Metallic sodium cations [Na^+] are diffused in the hydrated gel outside of the glass and in the solution, while the hydrogen ions [H^+] are diffused in the gel. This gel makes the pH electrode ion-selective: Hydrogen ions [H^+] cannot pass through the glass membrane of the pH electrode. Sodium ions [Na^+] pass through and cause a change in free energy, which the pH meter measures. A brief explanation of the theory on how electrodes function is included in the appendix at the end of the chapter.
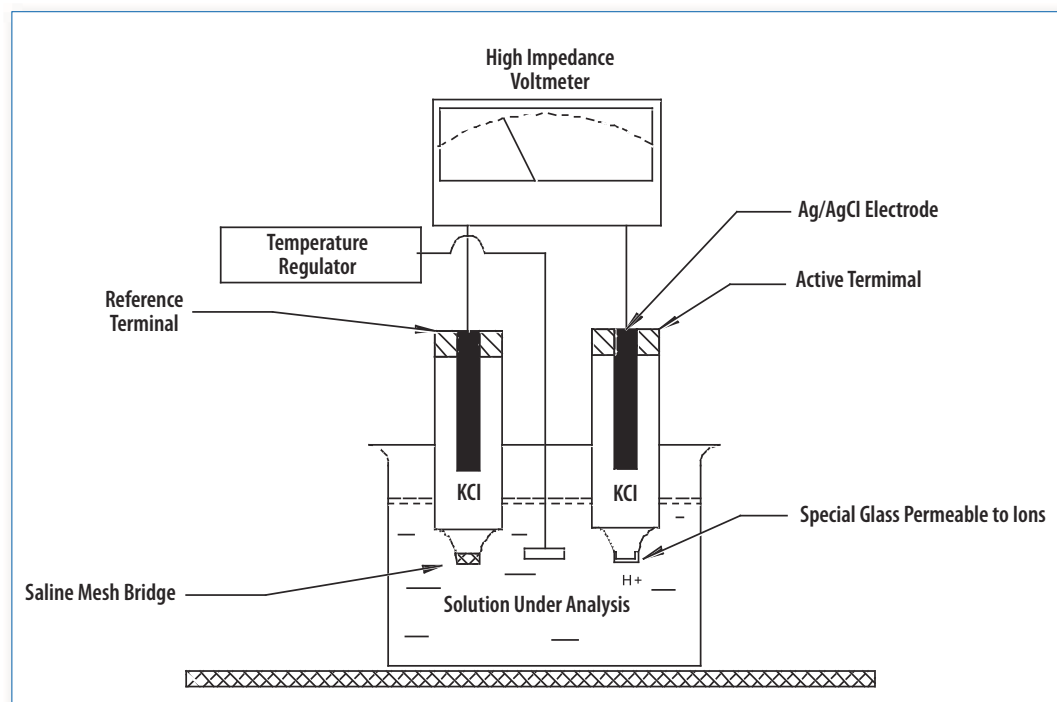
pH METER COMPONENTS
A pH meter generally has the following components:
1. *The body of the instrument containing the circuits, controls, connectors, display screens and measuring scales.* The following are among some of its most important components:
   a) *An ON and OFF switch.* Not all pH meters have an on and off switch. Some simply have a cord with a plug which allows it to be connected to a suitable electrical outlet.
   b) *Temperature control.* This control allows adjustments according to the temperature of the solution measured.
   c) *Calibration controls.* Depending on the design, pH meters possess one or two calibration buttons or dials. Normally these are identified by **Cal 1** and **Cal 2**. If the pH meter is calibrated using only one solution, the Cal 1 button is used; making sure that Cal 2 is set at a 100%. If the pH meter allows two point calibrations, two known pH solutions covering the range of pH to be measured are used. In this case, the two controls are used (Cal 1 and Cal 2). In special cases, a three-point calibration must be done (using three known pH solutions).
   d) *Mode selector.* The functions generally included in this control are:
      I. **Standby mode (0).** In this position the electrodes are protected from electrical currents. It is the position used for maintaining the equipment while stored.
      II. **pH mode.** In this position the equipment can take pH measurements after performing the required calibration procedures.

Figure 4. Diagram of a pH meter

III. **Millivolt mode (mV).** In this position the equipment is capable of performing millivoltage readings.

IV. **ATC mode.** The automatic temperature control mode is used when the pH is measured in solutions for which the temperature varies. This function requires the use of a special probe. Not all pH meters have this control.

2. *A combined electrode or probe.* This device must be stored in distilled water and stay connected to the measuring instrument. A combination electrode has a

reference electrode (also known as *Calomel* electrode) and an internal electrode, integrated into the same body. Its design varies depending on the manufacturer.

TYPICAL CIRCUIT

Figure 6 features a typical circuit adapted to the control system of the pH meter. Each manufacturer has its own designs and variations.
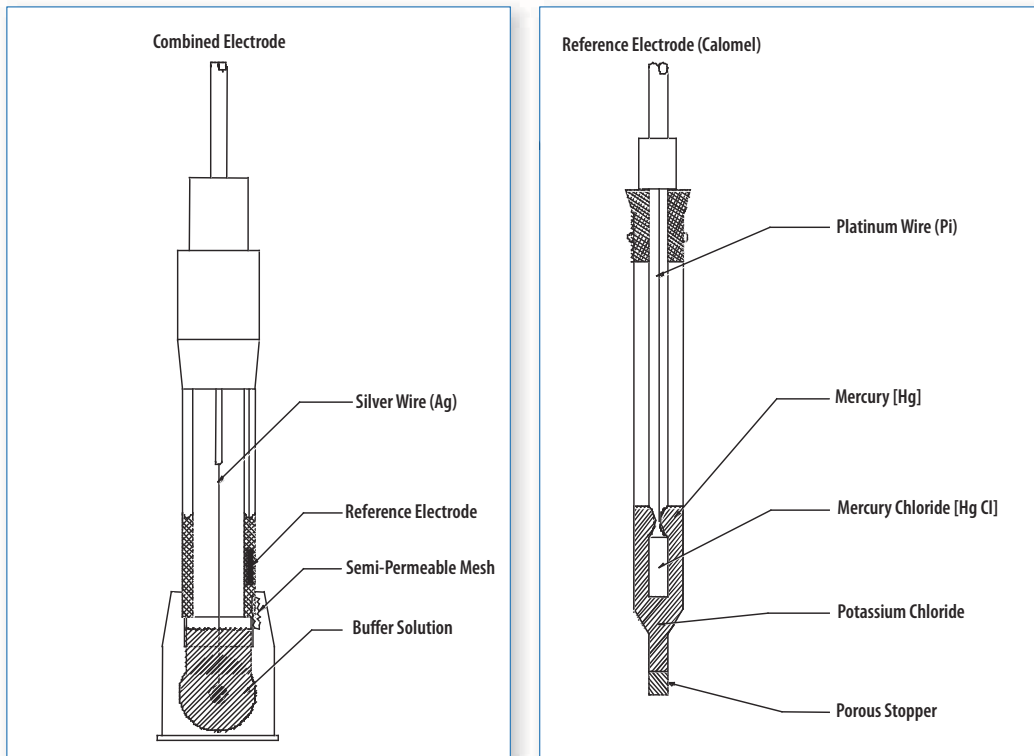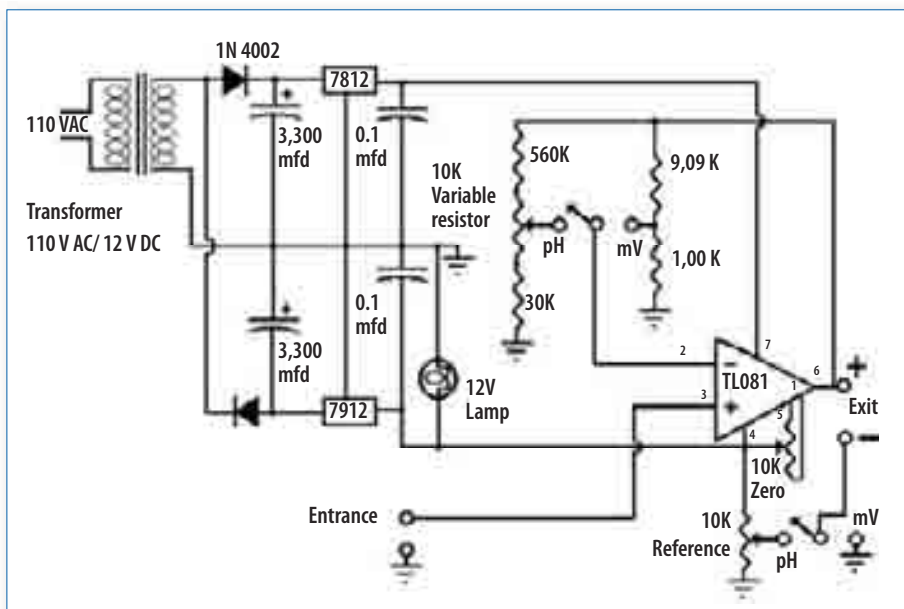
Figure 5. Types of electrodes

Figure 6. Example of a typical pH meter control circuit

Description of typical control circuit elements

System	Element	Description
Electric feeding and correction.	110 V/12 V AC transformer.*	A device converting the voltage of the 110 V to 12 V AC network.
	1N4002 rectifier diodes.	Diode controlling the type of wave and guaranteeing that is positive.
	Electrolyte condensers 3300 microfarads (μfd) (2).	Condensers absorbing the DC voltage to the diodes.
	Tri terminal regulators (7812, 7912).	A device regulating the voltage resulting from the interaction between diodes and condensers.
	0.1 microfarad (μfd) (2) electrolyte condensers.	Devices used to achieve stability at high frequency.
	12 V D C signal light.	Light indicating if the equipment is ON.
Measurement of pH and millivolts.	TL081 non-inverted type dual amplifier.	Millivolts circuits.
	(R1) 9.09 K Ω (ohm) resistors.	
	(R2) 1 K Ω (ohm) resistors.	
	(R3) 560 K Ω (ohm) resistors.	pH circuits.
	(R4) 10 K Ω(ohm) variable resistors.	
	(R5) 30 K Ω (ohm) resistors.	Ground resistance.
		The circuit gain is governed by means of the following equation: $Gain = 1 + (R3 + P x R4)/R5 + (1 - P) x R4$.
Outlet section.	Low cost DC voltmeter.	Permits readings in millivolts. The voltage read is 10 times that of the cell, allowing a resolution of 0.1 millivolts.
		The reading is done by using carbon/quinhydrone electrodes.

* Different voltage specifications are applicable in certain regions of the World.

INSTALLATION REQUIREMENTS

The pH meter works using electric current with the following characteristics.

Power: Single phase Voltage: 110 V or 220-230 V Frequencies; 50-60Hz depending on the World region.

There is also portable pH meters powered with batteries.

GENERAL CALIBRATION PROCEDURE

pH analyzers must be calibrated before use to guarantee the quality and accuracy of the readings following these procedures:

1. *One point calibration.* This is carried out for normal working conditions and for normal use. It uses one known pH reference solution.
2. *Two point calibration.* This is done prior to performing very precise measurements. It uses two known pH reference solutions. It is also done if the instrument is used sporadically and its maintenance is not carried out frequently.

Description of the process

Frequency: Daily

1. *Calibrate the pH meter using one known pH solution (one point calibration).*
   1.1 Connect the equipment to an electrical outlet with suitable voltage.
   1.2 Adjust the temperature selector to the environmental temperature.
   1.3 Adjust the meter.
   1.4 Remove the electrodes from the storage container. The electrodes must always be stored in a suitable solution. Some can be maintained in distilled water, others must be kept in a different solution as their manufacturers recommend[1]. If for some reason, the electrode becomes dry, it is necessary to soak it for at least 24 hours before use.
   1.5 Rinse the electrode with distilled water in an empty beaker.
   1.6 Dry the electrode with material able to absorb residual liquid on its surface, without impregnating the electrode. To avoid possible contamination, the electrodes must be rinsed between different solutions.

[1] Verify the type of buffer solution recommended by the electrode manufacturer.

2. ***Place electrodes in the calibration solution.***

   2.1 Submerge the electrode in the standardization solution in such a manner that its lower extremity does not touch the bottom of the beaker. This decreases the risk of breaking the electrode. If the test requires that the solution be kept in motion using the magnetic agitator, special care must be taken so that the agitation rod does not hit the electrode as this could break it. Buffer solution is used as a calibration solution, because its pH is known and therefore will still be maintained even if a little contamination occurs. In general, a solution of pH = 7 is used for this purpose[1].

3. ***Turn the functions selector from Standby position to pH position.***

   3.1 This action connects the electrode to the pH measuring scale in the pH meter.

   3.2 Adjust the meter to read the pH of the calibration solution using the button marked Cal 1. This enables the meter to read the pH of the calibration solution.

      For example: For a solution at pH = 7, the needle can oscillate slightly in units of 0.1 pH; on average, the reading should be 7. The reading of the meter (reading scale) should be done perpendicularly, to avoid or eliminate parallel-type errors (reading errors produced by the shadow of the meter's needle, visible on the mirror of the reading scale). The pH meter is then ready (calibrated), to carry out the correct pH readings.

   3.3. Put the functions selector in the Standby position.

4. ***Measuring the pH of a solution.***

   4.1 Remove the electrode from the calibration solution.

   4.2 Rinse the electrode with distilled water and dry it.

   4.3 Place the electrode in the solution of unknown pH.

   4.4 Turn the functions selector from the Standby position to the pH position.

   4.5 Read the pH of the solution on the meter's scale or the screen. Register the reading obtained on the control sheet.

   4.6 Turn the functions selector again to the Standby position.

      If it is necessary to measure the pH of more than one solution, repeat the previously described procedures, rinsing the probe with distilled water and drying with clean, lint-free paper between readings. When the pH has to be measured in numerous solutions, the pH meter must be calibrated frequently, following the steps previously described.

5. ***Turn off the pH meter.***

   5.1 Remove the electrode from the last solution analyzed.

   5.2 Rinse the electrode in distilled water and dry it with a drying material that will not penetrate it.

   5.3 Place the electrode in its storage container.

   5.4 Verify that the functions selector is in the Standby position.

   5.5 Activate the off switch or disconnect the feed cable, if it lacks this control.

   5.6 Clean the work area.

GENERAL MAINTENANCE OF THE pH METER

pH meters have two general maintenance procedures: one concerning the analyzer's body, the other for the pH detection probe (electrodes).

General maintenance procedures for the pH meter's body

Frequency: Every six months

1. Examine the exterior of the equipment and evaluate its general physical condition. Verify the cleanliness of the covers and their adjustments.

2. Test the connection cable and its system of connections. Check that they are in good condition and clean.

3. Examine the equipment controls. Verify that these are in good condition and activated without difficulty.

4. Verify that the meter is in good condition. To do this, the instrument must be disconnected from the electric feed line. Adjust the indicator needle to zero (0) using the adjustment screw generally found below the pivot of the indicator needle. If the equipment has an indicator screen, check that it is functioning normally.

5. Confirm that the on indicator (bulb or diode) operates normally.

6. Verify the state of the electrode carrying arm. Examine the electrode attachment and assembly mechanism to prevent the electrode from becoming loose. Check that the height adjustment operates correctly.

7. Check the batteries (if applicable); change them if necessary.

8. Test its function by measuring the pH of a known solution.

9. Inspect the ground connection and check for escaping current.

[1] Verify the type of calibration solution recommended by the electrode manufacturer.

BASIC MAINTENANCE OF THE ELECTRODE
Frequency: Every four months
The measuring or detector electrode requires periodic maintenance of the conducting solution to obtain precise readings.
The recommended steps for replacing the electrolyte solution are the following:
1. Remove the detector electrode from the storage buffer solution.
2. Rinse the detector electrode abundantly with distilled water.
3. Remove the upper cover of the detector electrode.
4. Fill the conduit surrounding the internal electrode with a saturated potassium chloride (KCl) solution. Use the syringe or applicator supplied with the KCl solution. Verify that the tip of the syringe does not touch the inside of the electrode.
5. Close the electrode with its cover. Rinse the electrode in distilled water.
6. Keep the electrode in storage buffer solution while not in use.

Cleaning of the electrode
The type of cleaning required for electrodes depends of the type of contaminant affecting it. The most common procedures are summarized next:
1. *General cleaning.* Soak the pH electrode in a 0.1 M HCl solution or 0.1 M HNO_3, for 20 minutes. Rinse with water.
2. *Removal of deposits and bacteria.* Soak the pH electrode in a diluted domestic bleach solution (e.g. 1%), for 10 minutes. Rinse abundantly with water.
3. *Cleaning oil and grease.* Rinse the pH electrode with a mild detergent or with methyl alcohol. Rinse with water.
4. *Cleaning of protein deposits.* Soak the pH electrode in 1% pepsin and 0.1 M HCl for 5 minutes. Rinse with water.

After carrying out each cleaning operation, rinse with deionised water and refill the reference electrode before use.

Other precautionary measures
1. Do not strike the electrode. Given that the structure is generally made of glass and very fragile, it is necessary to manipulate it very carefully, preventing it from being knocked off.
2. Remember that the electrode has a limited lifespan.
3. While not in use, keep the electrode inside the storage buffer solution.

TROUBLESHOOTING TABLE		
PROBLEM	**PROBABLE CAUSE**	**SOLUTION**
The pH meter shows unstable readings.	There are air bubbles in the electrode.	Soak the electrode to eliminate the bubbles.
	The electrode is dirty.	Clean the electrode and recalibrate.
	The electrode is not immersed.	Verify that the sample covers the tip of the electrode perfectly.
	The electrode is broken.	Replace the electrode.
The electrode's response is slow.	The electrode is dirty or greasy.	Clean the electrode and recalibrate.
The screen shows an error message.	Incorrect operating mode selected.	Verify the operation mode selected. Select a valid operation.
The screen shows a calibration or error message.	There is a calibration error.	Recalibrate the pH meter.
	The calibration of the buffer value is erroneous.	Verify the buffer values used.
	The electrode is dirty.	Clean and calibrate the electrode.
The pH meter is on, but there is no signal on the screen.*	The batteries are badly installed.	Verify the polarity of the batteries.
	The batteries are worn out.	Replace the batteries.
The battery indicator is flashing.*	The batteries are worn out.	Replace the batteries.

* Applicable to equipment equipped with batteries only.

BASIC DEFINITIONS

Buffer. A solution containing either a weak acid and its salt or, a weak base and its salt, which makes it resistant to changes in pH at a given temperature.

Calomel electrode. A reference electrode used with the active electrode for determining the pH of a solution. This electrode is constructed with a mercury base (Hg), a covering of dimercuric chloride (Hg_2Cl_2) and a potassium chloride solution of 0.1 M. It is represented as $Cl_2[Hg_2Cl_2, KCl]Hg$.

Dissociation. A phenomenon through which a break in the molecules occurs. As a result it produces electrically charged particles (ions).

Electrolyte. A solute which produces a conducting solution, e.g. NaCl (sodium chloride) and NH_4OH.

Gel. A semisolid substance (e.g. jelly) composed of a colloid (solid) dispersed in a liquid medium.

Ion. Neutral atom which gains or loses an electron. When the atom loses an electron, it becomes a positively charged ion, called a cation. If the atom gains or captures an electron, it becomes a negatively charged ion, called an anion.

Ion-sensitive electrode. A device which produces a difference in potential proportional to the concentration of an analyte.

Molarity. Number of Moles (M) in a substance in a litre of solution. (Number of moles of solute in a litre (L) of solution). The brackets around the ionic symbol indicate that it is treated as a molar concentration.

Mol. (abbreviation for molecule). A quantity of any substance whose mass expressed in grams is numerically equal to its atomic mass.

Mole (unit). The amount of a substance that contains as many atoms, molecules, ions, or other elementary units as the number of atoms in 0.012 kilogram of carbon 12. It corresponds to the number 6.0225×10^{23}, or Avogadro's number, also called gram molecule.
The mass in grams of this amount of a substance, numerically equal to the molecular weight of the substance, also called *gram-molecular weight.*

pH. Measurement of the concentration of the hydrogen ion (H^+) given in moles per litre (M) in a solution. The pH concept was proposed by Sørensen and Lindstrøm-Lang in 1909 to facilitate expressing very low ion concentrations. It is defined by the following equation:
$$pH = -\log [H^+] \quad \text{or} \quad [H^+] = 10^{-pH}$$

It measures the acidity of a solution. Example, in water the concentration of $[H^+]$ is 1.0×10^{-7} M resulting in pH = 7. This allows the range of concentrations from 1 to 10^{-14} M, to be expressed from zero (0) to 14. There are diverse systems for measuring the acidity of a solution. An acidic substance dissolved in water is capable of producing H^+ ions. A basic substance dissolved in water is capable of producing $[OH^-]$ (hydroxides) ions.

An acid substance has a greater quantity of ions $[H^+]$ than pure water; a basic substance shows greater quantities of ions $[OH^-]$ than pure water. The concentrations of substances are expressed in moles per litre.

In pure water, the ion concentration $[H^+]$ and $[OH^-]$ is 1.0×10^{-7} M, it is thus considered a neutral substance. In reality, it is a weak electrolyte that is dissociated following the following equation:
$$H_2O \leftrightarrows [H^+][OH^-]$$

In all aqueous solutions there is a balance expressed as:
$$\frac{[H^+][OH^-]}{H_2O} = K$$

If the solution is diluted, the concentration of the non-dissociated water can be considered constant:
$$[H^+][OH^-] = [H_2O]K = K_a$$

The new constant Ka is called a constant of dissociation or ionic product of water and its value is 1.0×10^{-14} at 25 °C.
$$[H^+][OH^-] = 1.0 \times 10^{-14}$$
$$X \times X = 1.0 \times 10^{-14}$$
$$X^2 = 1.0 \times 10^{-14}$$
$$X = 1.0 \times 10^{-7}$$

In pure water the concentrations of H^+ and OH^- are 1.0×10^{-7} M, a very low concentration, given that the molar concentration of water is 55.4 mol/litre.

Solution. Homogenous liquid mixture (with uniform properties) of two or more substances. It is characterized by the absence of chemical reactions among the components in the mixture. The component in greater proportion and generally in a liquid state is called solvent and that or those in a lesser quantity, the solutes.

Annex
The pH theory

pH electrodes ideally behave as an electrochemical cell and react to the concentration of ions [H^+]. This generates an electromotive force (EMF) which, according to the Nernst law is calculated using the following equation:

$$E = E° + \frac{RT}{nF} \ln a_{H^+}$$

Given that:

$$pH = - \ln a_{H^+}$$ where a is the effective concentration of ions (Activity)

If n = 1, the equation is then rewritten as:

$$E = E° - \frac{R'T}{F} pH$$

E° is a constant dependant on the temperature. If E° is substituted by E'T, the calibration will be more sensitive. Real electrodes do not always perform according to the Nernst equation. If the concept of sensibility (s) is introduced, the equation can be rewritten as:

$$E = E'T - s\frac{R'T}{F} pH$$

The values of E' and s are found when measuring the EMF in two solutions with known pH. S is the slope of E versus pH, while E' is found at the intersection with the axis y. When E' and s are known, the equation can be rewritten and the pH can be calculated as:

$$pH = \frac{E'T - E}{s\dfrac{R'T}{T}}$$